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(71) Applicant: GENERAL ELECTRIC COMPANY
Schenectady, NY 12345 (US)

(72) Inventors:
- Tjahjadi, Mahari
  Evansville, Indiana 47712 (US)
- Gallucci, Robert Russell
  Mount Vernon, Indiana 47620 (US)
- Blackburn, Kirk J.
  Mount Vernon, Indiana 47620 (US)
- George, Eric R.
  Slingerlands, New York 12159 (US)

(74) Representative: Szary, Anne Catherine, Dr. et al
London Patent Operation,
GE International, Inc.,
Essex House,
12-13 Essex Street
London WC2R 3AA (GB)

(54) Flame retardant polyamide composition

(57) Flame retarded resin molding compositions with enhanced electrical properties comprising a polyamide resin, a flame retarding amount of a halogenated flame retardant, a fiber glass and/or mineral filler, and an effective amount of a pyrophosphate, and optionally including reinforcing glass fibers or an olefinic polymer for enhancing electrical properties.

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Description

This invention relates to flame retarded resin molding compositions having improved electrical properties.

Background of the Invention

Resins such as polyamide-6,6 are used in molding compositions due to their many excellent properties, i.e. strength, solvent resistance, etc. In applications which require good electrical properties, molded parts may be exposed to severe conditions, such as exposure to electrical discharge or to excessive current leakage across its surface. These conditions require not only that the molded part have flame resistance, but also that the molded part have a high degree of resistance to carbonization upon exposure to high voltage, i.e. good track resistance and a high degree of resistance to electrical discharge.

However, it has been a problem that flame retarded polyamide resins have poor track resistance compared to the non-flame retarded resin. US Pat. No. 4,559,372 to Giroud-Abel describes a composition of comprising (i) a polyamide, (ii) a fireproofing amount of red phosphorus, and (iii) an effective amount of at least one lanthanide compound as having improved electrical properties. Other materials mentioned include the incorporation of cupric oxide and cadmium oxide for improved arc resistance. This focus of this patent is on the utilization of red phosphorus.

Hence, it is desirable to provide additional ingredients which can enhance the track resistance of glass fiber polyamide composition, especially flame retardant polyamide compositions.

Summary of the Invention

It is an object of the present invention to provide flame retarded, reinforced polyamide resin molding compositions, likewise, articles molded from them which have improved electrical properties.

Another object of the present invention is to provide flame retarded polyamide resin molded articles and the molding compositions which are suitable for molded electrical devices, such as electrical outlets, circuit breakers, switches, fuse holders, lamp sockets, distributor caps, or ignition coils.

According to the present invention, there are provided flame retarded resin molding compositions with enhanced electrical properties, particularly track resistance, which comprise a polyamide, a flame retarding amount of a halogenated flame retardant fiber glass and/or mineral filler, and an effective amount of a pyro/polyphosphate for improving the electrical properties. The pyro/polyphosphate may be a metal pyrophosphate, a metal polyphosphate, a metal acid pyrophosphate, or metal acid polyphosphate.

In accordance with another aspect of the present invention, an olefinic polymer is included in the composition, in addition to the pyro/polyphosphate for enhancing the electrical properties.

Description of the Preferred Embodiments

In accordance with the principles of the present invention, the combination of ingredients are selected so that the compositions are suitable for electrical devices and have improved Comparative Tracking Index (CTI). CTI is typically measured by UL-746A or ASTM-D3638-85 or IEC-112-3rd Publication. The method of this test is intended to indicate the relative behavior of solid electrical insulating materials with regard to their susceptibility to surface tracking when exposed under electrical stress to water and other contaminants from the surroundings. This method is especially suitable for testing synthetic resin moldings. Comparative Tracking Index [illegible] is determined under the conditions specified in this test method which will cause failure with the application of [illegible] drops of electrolyte to the specimen [illegible] is used as a measure of the susceptibility of the material to tracking.

Preferably the CTI of the final composition is greater than or equal to about [illegible] greater than about [illegible] volts. Typically, neat polyamide [illegible] has a CTI value of about [illegible] the addition of flame retardants and glass fibers tend to decrease the CTI value to about 275 [illegible] volts. Hence it is desirable to select the remaining ingredients so as to not detract from the desirable flame retardancy and mechanical properties but enhance the CTI of the final composition.

Preferably the desired flame retardancy is V-0 according to Underwriters Laboratories Test No. 94. In addition [illegible] CTI and flame retardancy, important properties include good mechanical properties, good processability [illegible] molding cycle times, good flow, and good insulation properties [illegible] reinforcing materials such [illegible] retardant, and strength

$$M^{1}_{x}H_{y}P_{n}O_{(3n+1)}$$

wherein M is a metal, x is a number from 1 to 12, y is a number from 0 to 12, n is a number from 2 to 10, z is a number from 1 to 5 and the sum of (xz)+y is equal to n+2. M is preferably a Group IA, IIA, IB or IIB metal and more preferably sodium or potassium.

These compounds include, for example, pyrophosphates of the form $Na_3HP_2O_7$, $K_2H_2P_2O_7$, $Na_3H_2P_3O_{10}$, $KNaH_2P_2O_7$ and $Na_2H_2P_2O_7$ or sodium hexameta phosphate, $Na_8P_6O_{19}$. Typically, the metal pyro/polyphosphates are hydrates and may be in powder form. Sodium acid pyrophosphate is the most preferred.

The pyro/polyphosphate is added to the flame retarded molding compositions in an amount effective to increase track resistance but not in such amount that other essential properties of the molding composition are substantially degraded. Preferably, the final composition comprises from about 0.5 to about 40, and more preferably from about 0.5 to about 20 percent of the pyro/polyphosphate for improving the CTI.

Additionally, it has been found that olefinic type polymers may be added to provide enhancement of the CTI. Typical olefinic type polymers are the addition polymers of olefins. Suitable olefins include ethylene, propylene, butylene, hexene and octene or their copolymers.

Polyolefins may be high density polyethylene (d=above 0.94), low density polyethylene (d=about 0.92), linear low density polyethylene (d=0.916-0.940) or polypropylene. The olefin polymers may be copolymers, including ethylene-propylene or ethylene-butylene copolymers and those containing acid or ester structural units derived, for instance, from acrylic acid, methacrylic acid, acrylic esters, methacrylic esters, alkyl vinyl esters or the like, most often in the amount of about 5-25%, preferably 10-25 percent by weight. Most preferred are copolymers of ethylene with ethyl acrylate or methacrylate.

Preferably, olefinic type polymers are included in the final composition in an amount from about 1 to about 10, and more preferably from about 3 to about 7 percent by weight of the final composition as an effective amount to improve the CTI.

Included in the resin compositions of the present invention are mineral filler materials which act with the pyro/polyphosphates to enhance the track resistance. The preferred mineral fillers enhance the CTI. Typical mineral fillers include metal sulfates, micas, clays such as alumino silicates and alumino magnesium silicate, talcs, glass flake, wollastonite, metal oxides such as titanium dioxide, zinc sulfide, ground quartz, and the like. Preferred mineral fillers are the talc, clays and metal sulfates. Typical silicates include calcium silicates such as Wollastonite, aluminum silicates such as Kaolin which is a clay material composed of fine-grained minerals, kaolinite, hydrated magnesium silicates known as Talc, silica and alumina type mineral materials, and Mica which is a hydrous aluminosilicate material. Clay is a hydrated aluminium silicate generalized by the formula $Al_2O_3SiO_2xH_2O$. Talc is a preferred mineral filler.

The metal sulfate salts as well as their hydrates are a preferred mineral filler. Preferred metal sulfate salts are the Group IA and Group IIA metal sulfates with barium, calcium and magnesium sulfates being preferred.

Barium sulfate which is non-toxic and insoluble in dilute acids is especially preferred. Barium sulfate may be in the form of the naturally occurring barytes or as synthetically derived barium sulfate using well known synthetic techniques. The particle size may vary from 0.5 to 50 microns, preferably from 1 to 15 microns and most preferably 8 microns.

In most applications, the pyro/polyphosphates, mineral filler and reinforcing material such as glass fibers, comprise the filler material, and desirably represent 5 to 70%, and preferably from 10 to 50% of the total weight percent of the composition. Based on the total weight of the composition, reinforcement material is preferably present in an amount from 5 to 30 percent by weight, mineral filler in an amount from 3 to 30 percent by weight and pyro/polyphosphate in an amount from 0.5 to 20 percent by weight.

To achieve desired stiffness, the reinforcing material [illegible] agent. As previously discussed, the inclusion of glass fiber may deleteriously [illegible] amounts are desirable so as [illegible] undermine the CTI.

The [illegible] filamentous glass [illegible] compositions ultimately to be employed for electrical uses, it is preferred to use fibrous glass filaments comprised of borosilicate glass that is relatively soda-free. This is known as "E" glass. The filaments are made by standard processes, e.g., by steam or air blowing, flame blowing and mechanical pulling. The preferred filaments for plastic reinforcement are made by mechanical pulling. The filament diameters preferably range from about [illegible] microns.

In preparing the molding compositions it is convenient to use the filamentous glass in the form of chopped strands of from about 1/8" to about 1/2" long. In articles molded from the compositions [illegible] even shorter lengths [illegible] filaments are typically

the weight of resin. A preferred range will be from about 5 to 15 percent.

Typically halogenated aromatic flame-retardants include tetrabromo[illegible]. A polycarbonate oligomer, poly-[illegible]phenyl ether, brominated polystyrene, brominated BPA polyepoxide, [illegible] imides, brominated polycarbonate, poly (haloaryl acrylate), poly (haloaryl methacrylate), or mixtures thereof. [illegible] acrylate) is preferred with the most preferably being poly (pentabromobenzyl acrylate). PBB-PA has been known for some time, and is a valuable flame-retardant material, useful in a number of synthetic resins. PBB-PA is prepared by the polymerization of pentabromobenzyl acrylate ester (PBB-MA). The PBB-PA polymeric flame retardant material is incorporated into the synthetic resin during processing to impart flame retardant characteristics.

Examples of other suitable flame retardants are brominated polystyrenes such as polydibromostyrene and polytribromostyrene, decabromobiphenyl ethane, tetrabromobiphenyl, brominated alpha, omega-alkylene-bis-phthalimides, e.g. N,N'-ethylene-bis-tetrabromophthalimide, oligomeric brominated [illegible], especially carbonates derived from tetrabromobisphenol A, which, if desired, are end-capped with phenoxy radicals, or with brominated phenoxy radicals, or brominated epoxy resins. Other aromatic carbonate flame retardants are set forth in U.S. Patent 4,636,544 to Hepp.

The flame retardants are typically used with a synergist, particularly [illegible] antimony compounds. Such compounds are widely available or can be made in known ways. Typical inorganic synergist compounds include Sb_2O_5, SbS_3 and the like. Especially preferred is antimony trioxide (Sb_2O_3). Synergists such as antimony oxides, are typically used at about 0.5 to 15, and more preferably from 1 to 6 percent by weight based on the weight percent of resin in the final composition.

Also, the final composition may contain polytetrafluoroethylene (PTFE) type resins or copolymers used to reduce dripping in flame retardant thermoplastics.

Suitable polyamide components include polyamide-6, polyamide-6,6, polyamide-11, polyamide-12, polyamide-4,6, polyamide-6,10 and polyamide-6,12, as well as polyamides prepared from terephthalic acid and/or isophthalic acid and trimethylhexamethylenediamine; from adipic acid and m-xylylenediamines; from adipic acid, azelaic acid, 2,2-bis-(p-aminocyclohexyl) propane, and from terephthalic acid and 4,4'-diaminodicyclohexylmethane. Mixtures and/or copolymers of two or more of the foregoing polyamides or prepolymers thereof, respectively, are also within the scope of the present invention.

Furthermore, the polyamides may be made by any known method, including the polymerization of a monoamino monocarboxylic acid or a lactam thereof having at least 2 carbon atoms between the amino and carboxylic acid group, of substantially equimolar proportions of a diamine which contains at least 2 carbon atoms between the amino groups and a dicarboxylic acid, or of a monoaminocarboxylic acid or a lactam thereof as defined above together with substantially equimolar proportions of a diamine and a dicarboxylic acid. The dicarboxylic acid may be used in the form of a functional derivative thereof, for example, a salt, an ester or acid chloride.

A detailed description of polyamides and polyamide precursor materials is provided in U.S. Pat. No. 4,755,566 to Yates. Other useful polyamides often referred to as "Nylons" are disclosed in U.S. Pat. Nos. 4,732,938 to Grant et al., 4,659,760 to Van der Meer, and 4,315,086 to Ueno et al., each also incorporated herein by reference. The polyamide used may also be one or more of those referred to as "toughened nylons", which are often prepared by blending one or more polyamides with one or more polymeric or copolymeric elastomeric toughening agents. Examples of these types of materials are given in U.S. Pat. Nos. 4,174,358, 4,474,927, 4,346,194, 4,251,644, 3,884,882, 4,147,740, all incorporated herein by reference, as well as in a publication by Gallucci et al., "Preparation and Reactions of Epoxy-Modified Polyethylene", J. APPL. POLY. SCI., V.27, PP. 425-437 (1982).

The preferred polyamides for this invention are polyamide-6, 6,6, 11 [illegible] with the most preferred being polyamide 6,6.

The polyamides used herein preferably have an intrinsic viscosity [illegible] as measured [illegible] 40 [illegible] mixture or similar solvent at [illegible].

Blends of various polyamide resins as the polyamide component [illegible] to about [illegible] parts by [illegible] preferred polyamides as set forth above and from about 99 to about [illegible] by weight other polyamides based on 100 parts by weight of both components combined.

Additional ingredients may include other thermoplastic resins in an amount up to about 50 percent by weight based on the weight of the formulation. Such other suitable thermoplastic resins which may be used include polyesters, acrylic and methacrylic polymers or copolymers, epoxy resins, polycarbonates, [illegible] polyphenylene oxide based resins such as polyphenylene oxide and blends of polyphenylene oxide and [illegible] polyethers, polyphenylene sulfides, polyetherketones, aliphatic polyketones, polysulfones, and [illegible]
[illegible]

Other ingredients employed in low amounts, typically less than 5 percent by weight of the total composition, include stabilizers, lubricants, colorants, plasticizers, nucleants, antioxidants and UV absorbers. These ingredients should be selected so as not to deleteriously affect the desired properties of the molded resin.

Although it is not essential, best results are obtained if the ingredients are precompounded, pelletized and then molded. Precompounding can be carried out in conventional equipment. For example, after predrying the polyamide resin, other ingredients, and, optionally, other additives and/or reinforcements, a single screw extruder is fed with a dry blend of the composition. On the other hand, a twin screw extrusion machine can be fed with resins and additives at the feed port and reinforcement down stream.

Portions of the blend can be precompounded and then, extruded with the remainder of the formulation, and cut or chopped into molding compounds, such as conventional granules, pellets, etc., by standard techniques.

The compositions can be molded in any equipment conventionally used for thermoplastic compositions. For example, good results will be obtained in an injection molding machine, e.g. of the 80 ton Van Dorn type, with conventional temperatures which depend on the particular thermoplastic utilized. If necessary, depending on the molding properties of the polyamide, the amount of additives and/or reinforcing filler and the rate of crystallization of the polyamide component, those skilled in the art will be able to make conventional adjustments in molding cycles to accommodate the composition.

Flammability tests were performed with the procedure of Underwriter's Laboratory Bulletin 94 entitled "Combustion Tests for Classification of Materials, UL-94." According to this procedure, the materials were classified as either UL-94 V-0, UL-94 V-1 or UL-94 V-2 on the basis of the tests results obtained for five samples. The criteria for each of these flammability classifications according to UL-94, are, briefly, as follows:

V-0: the average period of flaming and /or smoldering after removing the igniting flame should not exceed five seconds and none of the samples should produce drips of particles which ignite absorbent cotton.
V-1: the average period of flaming and/or smoldering after removing the igniting flame should not exceed twenty-five seconds and none of the samples should produce drips of particles which ignite absorbent cotton.
V-2: the average period of flaming and/or smoldering after removing the igniting flame should not exceed twenty-five seconds and the samples may produce drips of burning particles which ignite absorbent cotton.

The following examples illustrate the preparation of certain compositions within the scope of this invention. They are not to be construed to limit the invention in any manner whatsoever. All parts, except as otherwise indicated, are by weight.

Examples

The formulations shown below in Tables 1 were preblended and extruded in a 2.5 inch 30:1 L/D HPM Single Screw Extruder. The extrudate was cooled through a water bath prior to pelletizing. Test parts were injection molded in a 80 ton Van Dorn molding machine. The pellets were dried for 3-4 hours at 250°F in a forced air circulating oven prior to injection molding.

The control experiments labeled A-E showed low CTI. Compared to the control experiments, the formulations of the invention, labeled 1-7, containing pyro/polyphosphates and sulfates or minerals showed improved CTI. The pyro/polyphosphate are metal pyrophosphates, metal polyphosphates, metal acid pyrophosphates, or metal acid polyphosphates.

Formulation A was polyamide 6,6 resin plus 30 percent glass plus [illegible] ethylene copolymer and [illegible]. The flame retardant system was polybrominated [illegible] 275 volts.

Formulation B was Formulation A with [illegible] effects on the CTI which was improved to 350 volts.

Formulation 1 was Formulation B with 4% less talc and replaced by sodium acid pyrophosphate (SAPP). Talc and SAPP combination showed beneficial effects on the CTI which was improved to 375 volts.

Formulation 2 was Formulation 1 with 4.5% less talc and replaced by [illegible] ethylacrylate (EEA). Talc and EEA combination showed beneficial effects on the CTI which was improved to 4[illegible] volts.

Formulation 3 was similar to Formulation 1 with 4.5% added ethylene [illegible] acrylate (EEA). Talc, SAPP and EEA combination showed beneficial effects on the CTI which was improved to 4[illegible] volts.

Formulation C was polyamide 6 resin plus 30 percent glass plus flame retardant with [illegible] ethylene copolymer and [illegible]

Formulation 5 was similar to Formulation 4 with 4.5% added ethylene ethyl acrylate (EEA). Talc, SAPP and EEA combination showed beneficial effects on the CTI which was improved to 425 volts.

Formulation E was polyamide 6 resin plus 30 percent glass plus flame retardant without ethylene copolymer and fillers. The flame retardant system was bromo epoxy with antimony synergist. The CTI was 300 volts.

Formulation F was Formulation E with 10% less glass and 25% talc. This showed beneficial effects on the CTI which was improved to 375 volts.

Formulation 6 was Formulation F with 4% less talc and replaced by sodium acid pyrophosphate (SAPP). Talc and SAPP combination showed beneficial effects on the CTI which was improved to 425 volts.

Formulation 7 was similar to Formulation 6 with 4.5% added ethylene ethyl acrylate (EEA). Talc, SAPP and EEA combination showed beneficial effects on the CTI which was improved to 450 volts.

Articles which are molded from the formulated resins are suitable for use in various electrical devices such as electrical outlets, circuit breakers, switches, fuse holders, lamp sockets, distributor caps, enclosures or ignition coils. Such articles may be formed by conventional molding techniques.

ABLE 1

Material	A	B	1	2	3	C	D	4	5	E	F	6	7
SIN													
lyamide 6,6 - (1)	58.85	43.85	43.85	43.85	38.85								
lyamide 6 - (2)						58.85	43.85	43.85	38.85	56.60	41.60	41.60	36.60
ASS													
lass - (3)	30.00	20.00	20.00	20.00	20.00	30.00	20.00	20.00	20.00	30.00	20.00	20.00	20.00
SYNERGIST													
Acrylate - (4)	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00				
2O3 Conc - (5)	3.00	3.00	3.00	3.00	3.50	3.00	3.00	3.00	3.00				
Epoxy+Sb2O3 Conc. - (6)										13.25	13.25	13.25	13.25
eral													
		25.00	21.00	20.50	21.00		25.00	21.00	21.00		25.00	21.00	21.50
PP (7)			4.00		4.00			4.00	4.00			4.00	4.00
rs													
A - (8)				4.50	4.50				4.50				4.50
nox TM 1076 - (9)	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
4 @ 1.6mm	V-2	V-2	V-1	V-1	V-1	V-2	V-2	V-1	V-1	V-2	V-2	V-1	V-1
Volts	275	350	375	425	475	300	400	475	500	300	375	425	475

olyamide 6,6 resin
olyamide 6 resin
4 micron diameter glass
oly(pentabromobenzyl Acrylate) Mw 15,000
5% Sb2O3 and 15% olefinic binder
5% Brominated Epoxy and 25% Sb2O3 concentrate
odium Acid Pyrophosphate
olycopolymer of Ethylene with 18% Ethyl Acrylate
indered Phenol Anti Oxidant

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Claims

1. A flame retarded resin molding composition with enhanced electrical properties comprising a polyamide resin, a flame retarding amount of a halogenated flame retardant, fiber glass and a mineral filler, and an effective amount of a pyro polyphosphate selected from the group consisting of metal pyrophosphates, metal polyphosphates, metal acid pyrophosphates, metal acid polyphosphates and mixtures thereof.

2. A flame retarded resin molding composition according to claim 1 wherein said pyro polyphosphate has the formula $M_xH_yP_nO_{3n+1}$ wherein M is a metal, x is from 1 to 5, x is a number from 1 to 12, y is a number from 0 to 12, n is a number from 2 to 10.

3. A flame retarded resin molding composition according to claim 2 wherein the CTI of the final composition is greater than about 400 volts.

4. A flame retarded resin molding composition according to claim 1 wherein said flame retardancy is V-O according to Underwriters Laboratories Test No. 94.

5. A flame retarded resin molding composition according to claim 1 wherein said flame retardant is a poly (haloaryl-methacrylate), halogenated polystyrene or a poly (haloarylacrylate) flame retardant.

6. A flame retarded resin molding composition according to claim 1 wherein said resin molding composition includes a reinforcing material.

7. A flame retarded resin molding composition according to claim 6, wherein said pyropolyphosphate, said mineral filler, and reinforcing material such as glass fiber comprise the filler content of said resin and said filler content comprises from 10 to 50% of the total weight percent of the composition.

8. A flame retarded resin molding composition according to claim 7 wherein based on the total weight of the composition, said glass fiber is present in an amount from 5 to 30 percent by weight, mineral filler is present in an amount from 3 to 30 percent by weight and said pyrobo yphosphate is present in an amount from 0.5 to 20 percent by weight wherein said weight percents are based on the total weight of said composition.

9. A flame retarded resin molding composition according to claim 1 additionally including an effective amount of an olefinic polymer for improving electrical properties.

10. An article molded from the flame retarded resin molding composition according to claim 1.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 30 0624

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	FR 1 545 754 A (URGESI) 7 October 1968		C08K5/00 C08K5/32
A	FR 1 460 674 A (FIRESTONE) 9 February 1967		
A	FR 1 464 645 A (FIRESTONE) 16 March 1967		
A	EP 0 183 195 A (BASF AG) 4 June 1986		

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C08K

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 May 1998	Leroy, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document